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## 54 Organoclays

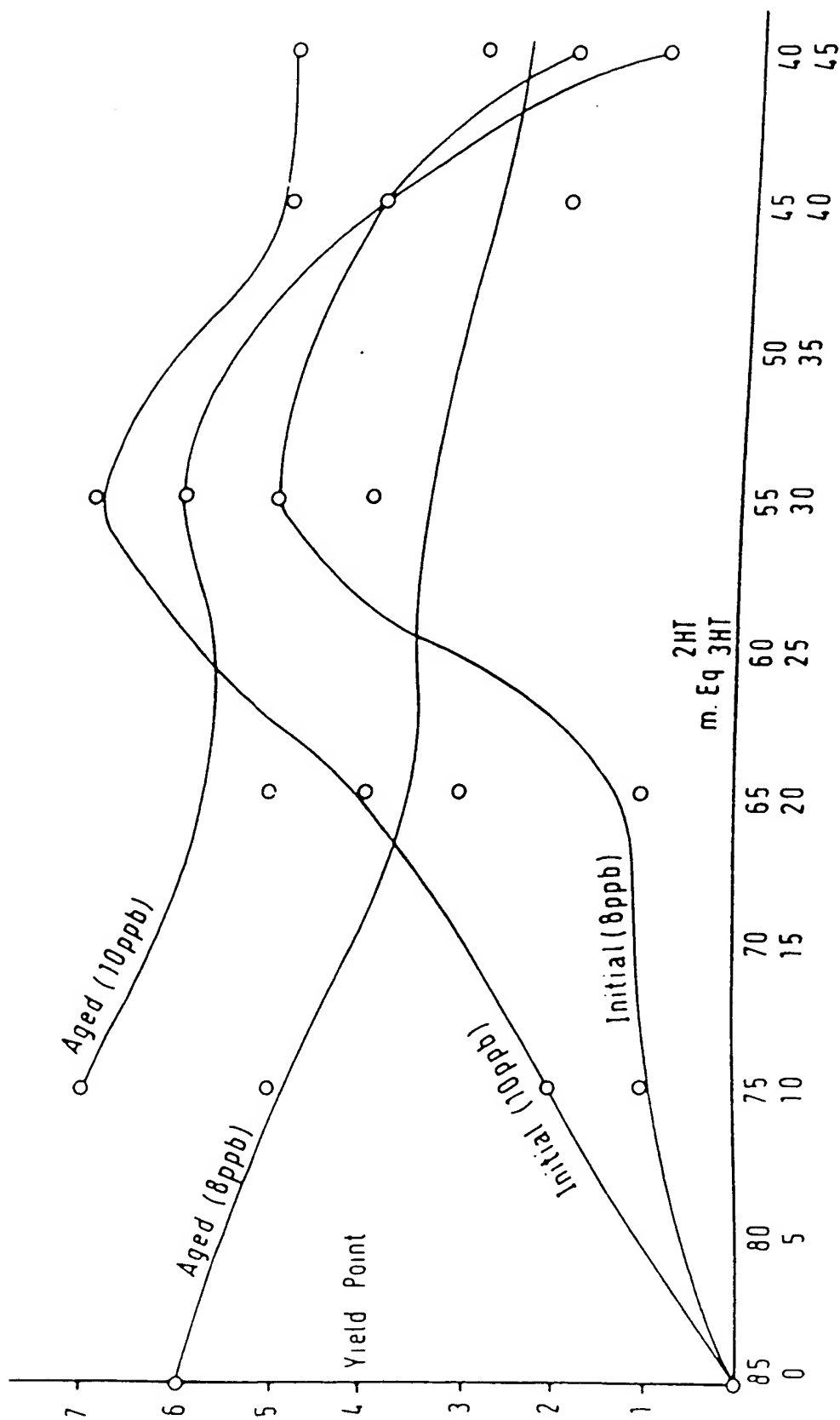
57 An organoclay material adapted specifically for use in a given system is selected by testing the system with organoclays made using a range of quaternary ammonium compounds having varying average carbon chain lengths, particularly by reacting suitable clays with mixed quaternary ammonium compounds, in order to determine a optimum C to N ratio in such quaternary ammonium compounds for that system. An organoclay is then manufactured substantially in accordance with the optimum ratio by utilising one or more selected quaternary ammonium compounds designed substantially to achieve the optimum C to N ratio or a single quaternary ammonium compound which affords said C to N ratio.

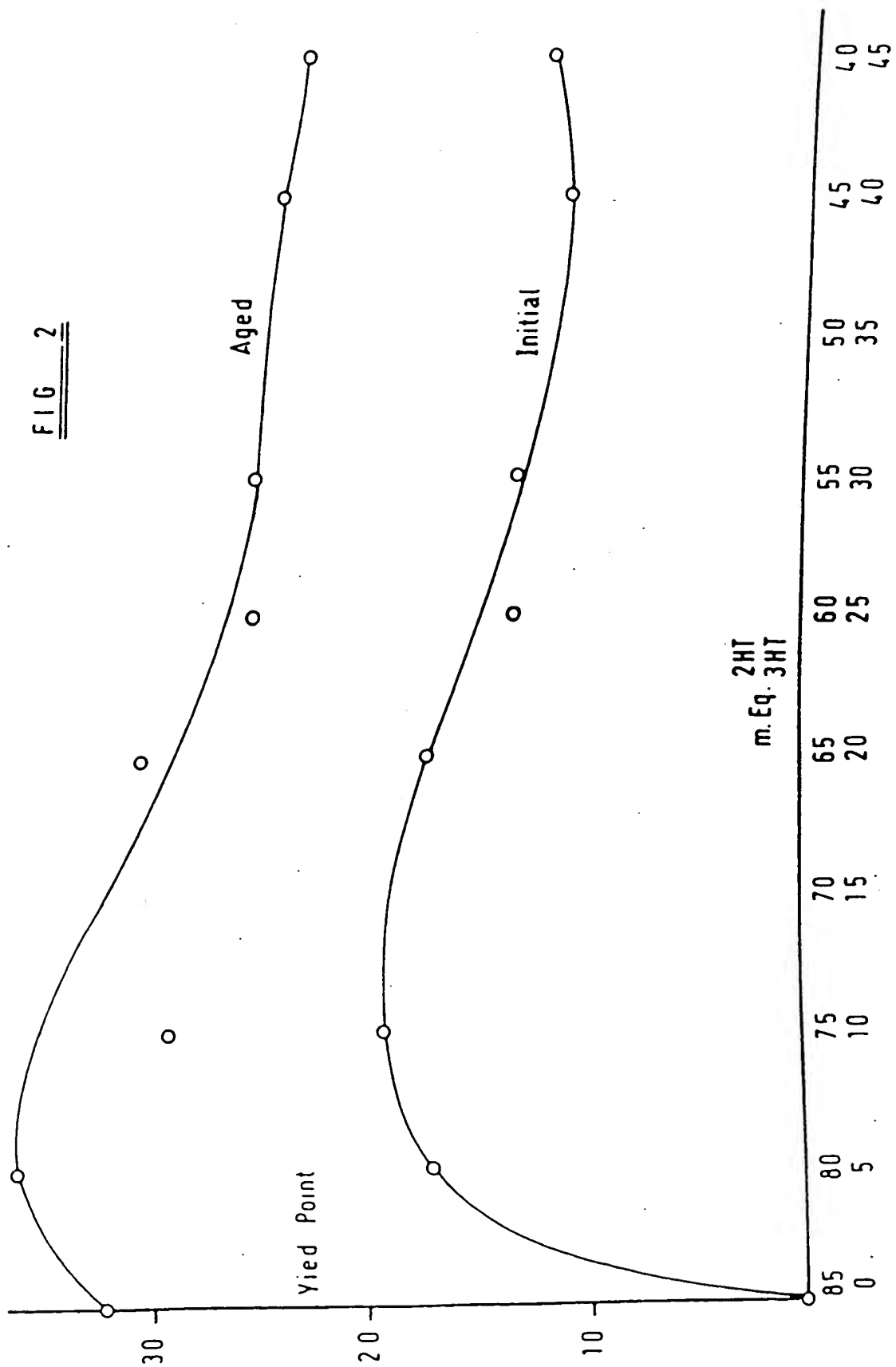
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FIG 1





## SPECIFICATION

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## Organoclays

5 *Description of the invention*

This invention relates to organoclay materials, that is to say materials formed by the reaction of a smectite clay, such as bentonite, hectorite or montmorillonite, with a quaternary ammonium compound. These materials are used, for example, as additives for modifying or controlling thixotropic properties of various fluids, such as paints and drilling muds. The purpose for which organoclays are incorporated in such fluids is generally to increase the initial yield point, i.e. the viscosity at zero shear as extrapolated from measurements made at various shear rates.

The quaternary ammonium compounds used may vary according to the solvent systems into which the organoclay is to be incorporated. For polar solvent systems e.g. those based on alcohols, the compound used may for example be a  $C_{12}$  alkyl ammonium compound. For aromatic solvent systems e.g. toluene based, a di-methyl hydrogenated tallow benzyl ammonium compound may be used. For aliphatic solvent systems, e.g. white spirit based, a di-methyl di-hydrogenated tallow ammonium compound may be used. However, for systems having a very low aromatic content, such as highly refined "white oils", such hydrogenated tallow compounds are slow to solvate.

In general, some improvement can be obtained by increasing the carbon chain content of the quaternary compound, for example by utilising trihydrogenated tallow instead of di-hydrogenated tallow compounds. However, the use of such more complex compounds inevitably incurs significant increased costs.

Tests which we have carried out to determine whether any useful advantage can be obtained by replacing only part of the di-hydrogenated tallow compound by the corresponding tri-hydrogenated tallow compound have indicated not only that the use of a mixture of such compounds can indeed be beneficial, but, surprisingly, also that over a range of ratios the results may be better than those obtained when using either the dihydrogenated tallow compound or the tri-hydrogenated compound alone in equivalent quantities. Further tests have shown that the ratio of the two compounds which provides the greatest improvement is dependent at least on the system in which the organoclay material is used.

The present invention resides broadly in the concept of forming an organoclay material by reacting a mixture of different quaternary ammonium compounds, having differing average carbon chain lengths, with a smectite clay, wherein the ratio of the different compounds is adjusted to an optimum value relative to the system in which the organoclay is to be used. A similar result does not appear to be achieved by blending two different organoclays which are each made using a different quaternary compound, but a similar result may be obtained by the use of a single quaternary compound having an optimised average carbon chain length.

Thus, from one aspect, the present invention resides in a method of producing an organoclay material adapted specifically for use in a given system by testing the system with organoclays made using a range of quaternary ammonium compounds having varying average carbon chain lengths in order to determine the optimum C to N ratio in such quaternary ammonium compounds for that system, and then manufacturing an organoclay substantially in accordance with that optimum ratio by utilising one or more selected quaternary ammonium compounds designed substantially to achieve said optimum C to N ratio.

In a solvent system an organoclay under suitable conditions will disperse and solvate, and the solvated organoclay will interact to give the system a structure which determines its thixotropic properties. The present invention is concerned primarily with organoclays for use in oil mud systems for use as drilling fluids, and it is believed that for different types of oil, the rate of solvation of the organoclay will differ.

In order to increase the rate of solvation the organic component of the organoclay should be increased in size where the solvent is one in which solvation is relatively difficult as compared with one in which solvation is relatively easy. Solvent systems based on heavy oils, such as diesel oil provide relatively easy solvation, whereas solvent systems based on more highly purified, less aromatic oils ("white oils") are more difficult to solvate, and the present invention is concerned with the preparation of organoclays mainly intended for use in the latter type of system.

Tests carried out to show the effect of increasing the organic content of the organoclay by using greater quantities of quaternary ammonium compounds, which therefore utilises a higher milli-equivalent of the ion exchange sites on the clay, have shown that a good initial yield may be obtained in this way in white oil systems, but the improvement is not maintained after ageing of the system.

Essentially, the present invention is concerned with the possibility of increasing the total organic component of the organoclay without simultaneously increasing the utilisation of exchange sites on the clay. However, as mentioned above, tests utilising equivalent quantities of tri-hydrogenated tallow ammonium compounds instead of di-hydrogenated tallow compounds have produced results which are inferior to tests utilising mixtures of such compounds, which thus suggests that there is an optimum carbon content which can be determined experimentally for any given system.

The following examples and tests illustrate the way in which variation of the carbon content of the quaternary ammonium compounds used in the preparation of organoclays affects the properties of drilling muds in which such organoclays are incorporated.

**Example 1**

An organoclay was made by a dry process using a Wyoming Bentonite clay with 40 m Eq. trihydrogenated tallow dimethyl ammonium chloride (3HT) and 45 m Eq. dihydrogenated tallow dimethyl ammonium chloride (2HT).

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**Test 1**

The product was dried and milled and tested by incorporation in a commercially available drilling mud (system a) of the white oil type in a quantity of 8 ppb. The yield point of the mud system was then determined both before and after ageing by using a Fann 35SA viscometer and taking readings at various rpm. The plastic viscosity PV is calculated as the difference between the 600 rpm and 300 rpm reading and the yield point YP is calculated as the difference between the 300 rpm reading and the PV value. The yield point should have a high value, but the ratio of PV to YP should be low.

The results were as follows:-

Test	600 300	200 100	6 3	PV	YP
1 (initial)	49 30	23 16	6 5	19	11
(aged)	76 50	32 29	12 10	26	24

Based purely on the number of hydrogenated tallow chains, if all the quaternary compound was the 2HT compound, the m.Eq. exchange capacity of the organoclay used in Test 1 would be  $45 + (1.5 \times 40) = 105$ . However, only 85 m Eq. of the active sites were used and the mixture appeared to work well in the system tested.

**Test 1A**

For comparison a standard organoclay including only 2HT was tested in the same mud system at the equivalent calculated level (105 m.Eq) with the following results:-

Test	600 300	200 100	6 3	PV	YP
1A (initial)	40 20	14 8	2 1	20	0
(aged)	102 67	53 38	15 13	35	32

Increasing the carbon content of the organoclay without a corresponding increase in the usage of exchange sites on the clay thus gave a product that has a good initial yield and will not collapse on ageing. The organoclay of Example 1 was also tested in two other mud systems as follows:-

(b) a system having a no lime or styrene polybutadiene emulsion and a different emulsifier system to that of mud system a;

(c) the mud system a as used in Test 1 but without styrene polybutadiene emulsion which is normally used in that system to enhance the organoclay performance.

Tests were carried out using these two mud systems with the organoclay made in accordance with Example 1 and the standard organoclay as used in Test 1A at various levels as follows:-

Test	Mud System	Organoclay	Concentration (ppb)
2	b	Ex. 1	10
2A	b	Std.	10
3	b	Ex. 1	12
3A	b	Std.	12
4	c	Ex. 1	8
4A	c	Std.	8

The results were as follows:-

Test	600 300	200 100	6 3	PV	YP
2 (initial)	47 26	18 11	2 1	21	5
(aged)	67 33	23 13	2 1	29	4
2A (initial)	30 15	10 5	1 0	15	0
(aged)	56 34	26 15	4 3	24	10
3 (initial)	63 38	27 15	3 2	23	2
(aged)	84 47	31 16	4 3	37	3
3A (initial)	34 17	11 5	1 0	17	0
(aged)	56 23	17 12	5 4	13	10
4 (initial)	44 27	21 14	5 4	17	11
(aged)	65 32	25 16	5 4	23	12

These results show that in mud system *c* (that is to say system *a* without the usual styrene butadiene polymer emulsion) gave good results despite the omission of the styrene butadiene polymer, whereas in system *b* good results were obtained at somewhat higher concentrations.

To test the effect of varying the ratio of 2HT to 3HT a range of further organoclays were made by the same process as for Example 1, but using different proportions of 2HT and 3HT to give a total theoretical m.Eq. of 85 in each case. The ratios of 2HT to 3HT used in Examples II to V were as follows:-

	Example No.	m.Eq.2HT	m.Eq.3HT	
10	Example II	40	45	10
	Example III	55	30	
	Example IV	65	20	
	Example V	75	10	

The product of Examples II to V were tested in the mud system *b* as used in tests 2 and 3 at 8 and 10 ppb, as follows:-

	Test	System	Organoclay	Concentration ppb	
20	5	<i>b</i>	Example II	8	20
	6	<i>b</i>	Example II	10	
	7	<i>b</i>	Example III	8	
	8	<i>b</i>	Example III	10	
	9	<i>b</i>	Example IV	8	
25	10	<i>b</i>	Example IV	10	25
	11	<i>b</i>	Example V	8	
	12	<i>b</i>	Example V	10	

The results were as follows:-

	Test	600 300	200 100	6 3	PV	YP	
30	5(Initial)	30 20	13 7	1 0	18	2	30
	(aged)	47 25	17 9	1 1	22	3	
35	6(Initial)	45 25	18 10	2 1	20	5	35
	(aged)	51 26	18 10	1 1	25	1	
	7(Initial)	29 22	15 3	1 1	17	5	
	(aged)	52 28	20 9	2 1	24	4	
	8(Initial)	47 27	19 11	2 1	20	7	
40	(aged)	62 34	24 13	2 1	28	6	40
	9(Initial)	35 18	12 6	1 1	17	1	
	(aged)	51 27	19 11	2 1	24	3	
	10(Initial)	40 25	14 8	1 1	18	4	
	(aged)	59 32	23 13	2 1	27	5	
45	11(Initial)	31 16	10 5	1 1	15	1	45
	(aged)	47 26	19 11	2 1	21	5	
	12(Initial)	38 20	13 7	1 1	18	2	
	(aged)	59 35	24 14	3 2	26	7	

The results of tests 5 to 12 are plotted in Figure 1. From this it appears that in this system an optimum value of initial yield is obtained using an organoclay made with a 3HT/2HT ratio of 30 to 55, but at this ratio a drop in yield is observed on ageing and it would appear that if initial and aged yields are taken into account together, the optimum ratio is likely to be in the region of 25 to 60 for system *b* although the results of tests 9 and 10 appear to be somewhat anomalous.

The products of Examples II to V were also tested in mud system *a*, as used in Test 1, together with the products of further Examples VI and VII of organoclays made as in Example I but using proportions of 2HT and 3HT as follows:-

	Example No.	m.Eq.2HT	m.Eq.3HT	
60	VI	60	25	60
	VII	30	55	

In all cases these organoclays were tested in mud systems *a* at a concentration of 8ppb as follows:-

	Test	System	Organoclay
5	13	a	Example II
	14	a	Example III
	15	a	Example IV
	16	a	Example V
	17	a	Example VI
10	18	a	Example VII

The results were as follows:-

	Test	600 300	200 100	6 3	PV	YP
15	13(initial)	53.32	25.17	7.6	20	12
	(aged)	81.52	41.29	12.10	29	23
	14(initial)	55.34	26.18	6.5	21	12
	(aged)	83.54	43.29	12.10	29	25
20	15(initial)	68.43	33.22	6.5	25	17
	(aged)	106.68	54.38	15.13	38	30
	16(initial)	73.46	37.25	6.5	27	19
	(aged)	99.64	49.35	12.11	35	29
	17(initial)	55.34	36.18	6.4	21	13
	(aged)	83.54	44.31	14.11	29	25
25	18(initial)	67.42	33.21	5.4	25	17
	(aged)	112.74	58.38	13.11	35	36

The results of tests 13 to 18 are shown in Figure 2, from which it is clear that for system *a* the optimum ratio appears to be in the region of 5/80 3HT to 2HT.

30 If the average carbon chain length of the hydrogenated tallow radical is assumed to be 17.16 then the average number of carbon atoms in one molecule of 2HT (i.e. the C to N ratio) will be 36.32 (including methyl Cl) whereas for 3HT it will be 52.48. For a mixed system in which the 3HT/2HT ratio is 5/80, the average C to N ratio will thus be 37.27, whilst for a mixed system in which the 3HT/2HT ratio is 25/60, the average value will be 41.07.

35 It will be seen that in this way it is possible to calculate an optimum C to N ratio for any particular system, by trials using varying ratios of quaternary ammonium compounds differing in carbon content. In this way, the optimum C to N ratio for the system under investigation can be determined and in production that ratio can be maintained by using an organoclay made by reacting the basic clay with the different quaternary compounds in the optimum ratio as determined.

40 Whilst it may be thought that it would also be possible to obtain similar results by utilising mixtures of different organoclays, each made wholly using one of the tested quaternary compounds, the organoclays being mixed in the proportions necessary to achieve the optimum C to N ratio as determined, further tests have indicated otherwise.

Tests 19 to 23 were carried out in mud system *a* using mixtures of organoclays as follows:-

	Test	System	3HT organoclay* (ppb)	2HT organoclay* (ppb)
45	19	a	8	0
	20	a	4	4
50	21	a	2	6
	22	a	1	7

\*85 m Eq

The results were as follows:-

	Test	600 300	200 100	6 3	PV	YP
55	19(initial)	35.22	16.11	4.4	13	9
	(aged)	48.30	23.15	7.6	18	12
60	20(initial)	35.20	15.9	3.3	15	5
	(aged)	71.45	74.23	11.10	25	19
	21(initial)	35.19	14.9	2.2	16	3
	(aged)	73.46	35.23	9.8	27	19
	22(initial)	41.22	17.11	3.2	19	3
65	(aged)	36.55	42.28	10.9	32	24

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Whilst these results suggest that there may be a slight peak at the same ratio as determined by Tests 13 to 18 in this mud system, the absolute values of yield point are significantly lower for both initial and aged tests

It is possible that the results obtained utilising an organoclay made using a single quaternary ammonium compound chosen to have an average C to N ratio which corresponds closely to the optimum C to N ratio as determined may be more closely similar to those being organoclays made by reacting a mixture of quaternary compounds with a smectite clay. Thus, for example, a specific ratio of 3HT to 2HT may correspond to the same C to N ratio as that of a single specific compound which would behave similarly.

Tests were accordingly carried out to evaluate this possibility, and to check the effect of attaining the same average C to N ratio by using the appropriate proportions of different quaternary compounds. For this purpose a range of further organoclays were made using 2HT and 3HT, HT (trimethyl hydrogenated tallow ammonium chloride) and 3HT, and 2HTB (methyl di-hydrogenated tallow benzyl ammonium chloride) as follows:-

Example No.	m.Eq.2HT	m.Eq.3HT	m.Eq.HT	m.Eq.2HTB	av.mol.wt.
VIII	53	29	—	—	655
IX	—	55	27	—	652
X	—	—	—	82	656

As will be observed in each of these examples the total m.Eq. of quaternary ammonium compound was 82 and the average molecular weight is substantially constant, representing a C to N ratio of approximately 41 to 42 in each case.

The organoclays of examples VIII to X were tested at 8ppb in a drilling mud composition containing a polymer emulsion in tests 23 to 25 as follows:-

Test	Organoclay	600 300	200 100	6 3	PV	YP
23(initial)	Ex.VIII	64 43	35 24	11 10	21	22
(aged)	—	87 55	43 30	15 14	32	23
24(initial)	Ex.IX	62 41	34 24	11 10	21	20
(aged)	—	80 52	41 29	15 14	28	24
25(initial)	Ex.X	69 46	36 25	9 8	23	23
(aged)	—	96 60	54 39	18 7	36	24

It can be seen that the initial yield point in each case is substantially identical and that the aged or final yield point in each case is also substantially identical, suggesting that it is the average C to N ratio which is responsible for the properties of the organoclay in this respect, regardless of whether the chosen average value is achieved by mixing 2HT and 3HT or 3HT and HT in the appropriate portions or by using a single compound 2HTB of the same molecular weight.

Further tests were carried out using these organoclays in the same drilling mud without polymer emulsion at 10ppb organoclay in tests 26 to 28 and 8ppb organoclay in tests 29 to 31 as follows:-

Test	Organoclay	600 300	200 100	6 3	PV	YP
26(initial)	Ex.VIII	58 38	28 20	8 7	20	18
(aged)	—	100 65	48 30	8 7	35	30
27(initial)	Ex.IX	82 51	46 34	17 15	31	20
(aged)	—	114 74	56 36	12 11	40	34
28(initial)	Ex.X	65 41	32 22	9 8	24	17
(aged)	—	102 64	43 27	7 6	38	26
29(initial)	Ex.VIII	46 29	20 15	6 5	17	12
(aged)	—	80 52	41 29	14 13	28	24
30(initial)	IX	50 31	27 22	8 7	19	12
(aged)	—	80 54	44 32	17 16	26	28
31(initial)	Ex.X	49 30	24 16	7 6	19	11
(aged)	—	71 46	34 23	10 9	25	21

Again the test results do not differ significantly according to the organoclay used with regard to the values of initial yield point, but there is rather more variation in final yield point value in the absence of emulsion at both levels of organoclay, and these tests also point to the equivalence of 2HTB in this system with mixtures of 2HT and 3HT or 3HT and HT affording the same average molecular weight

As a further test of the equivalence of mixed quaternary compounds and quaternary compounds of the same molecular weight or C to N ratio an organoclay was prepared using a mixture of HT and 3HT in proportions such as to give an average theoretical molecular weight of 576, i.e. that of 2HT, and compared with an organoclay made using an equivalent amount of 2HT alone with the following results:-



Test:	Organoclay	600 300	200 100	6 3	PV	YP
32	HT 3HT	33 20	14 8	2 1	13	7
33	2HT	37 22	15 9	2 1	15	7

Again the equivalence of the results is evident.

The features disclosed in the foregoing description, or in the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed results, or the class or group of substances or compositions, is appropriate, may, separately or any combination of such features, be utilized for realising the invention in diverse forms thereof.

#### CLAIMS

1. An organoclay material formed by reacting a mixture of different quaternary ammonium compounds, having differing average carbon chain lengths, with a smectite clay, wherein the ratio of the different compounds is adjusted to an optimum value relative to the system in which the organoclay is to be used.
2. A method of producing an organoclay material adapted specifically for use in a given system by testing the system with organoclays made using a range of quaternary ammonium compounds having varying average carbon lengths in order to determine the optimum C to N ratio in such quaternary ammonium compounds for that system, and then manufacturing an organoclay substantially in accordance with that optimum ratio.
3. A method according to Claim 2 wherein the system is tested with organoclays made using mixtures of quaternary ammonium compounds, each having differing average carbon chain lengths, so as to provide a range of C to N ratios.
4. A method according to Claim 2 or Claim 3 wherein the organoclay is manufactured utilising a mixture of quaternary ammonium compounds selected to afford substantially said optimum C to N ratio.
5. A method according to Claim 2 or Claim 3 wherein said organoclay is manufactured utilising a selected single quaternary ammonium compound affording substantially said optimum C to N ratio.
6. A method according to Claim 3 or Claim 4 wherein the mixture of quaternary ammonium compounds comprises compounds having differing numbers of long chain carbon radicals or the N atom of the molecule.
7. A method according to Claim 6 utilising mixtures of dimethyl di-hydrogenated tallow ammonium and methyl tri-hydrogenated tallow ammonium cations.
8. A method according to Claim 6 utilising mixtures of methyl tri-hydrogenated tallow ammonium and tri-methyl hydrogenated tallow ammonium cations.
9. A method according to Claim 5 utilising methyl di-hydrogenated tallow benzyl ammonium cations.

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